

**METHOD FOR IMPROVING THE OZONE STABILITY OF AN INKJET
RECORDING ELEMENT
FIELD OF THE INVENTION**

The present invention relates to a method for improving the ozone stability of an inkjet recording element.

Digital photography has been growing fast for several years and the general public now has access to efficient and reasonably priced digital cameras. Therefore people are seeking to be able to produce photographic prints from a simple computer and its printer, with the best possible quality.

Many printers, especially those linked to personal office automation, use the inkjet printing technique. There are two major families of inkjet printing techniques: continuous jet and drop-on-demand.

Continuous jet is the simpler system. Pressurized ink (3.10^5 Pa) is forced to go through one or more nozzles so that the ink is transformed into a flow of droplets. In order to obtain the most regular possible sizes and spaces between drops, regular pressure pulses are sent using for example a piezoelectric crystal in contact with the ink with high frequency (up to 1 MHz) alternating current (AC) power supply. So that a message can be printed using a single nozzle, every drop must be individually controlled and directed. Electrostatic energy is used for this: an electrode is placed around the ink jet at the place where drops form. The jet is charged by induction and every drop henceforth carries a charge whose value depends on the applied voltage. The drops then pass between two deflecting plates charged with the opposite sign and then follow a given direction, the amplitude of the movement being proportional to the charge carried by each of the plates. To prevent other drops from reaching the paper, they are left uncharged: so, instead of going to the support they continue their path without being deflected and go directly into a container. The ink is then filtered and can be reused.

The other category of inkjet printer is drop-on-demand (DOD). This constitutes the base of inkjet printers used in office automation. With this method, the pressure in the ink cartridge is not maintained constant but is applied when a character has to be formed. In one widespread system there is a row of 12 open

nozzles, each of them being activated with a piezoelectric crystal. The ink contained in the head is given a pulse: the piezo element contracts with an electric voltage, which causes a decrease of volume, leading to the expulsion of the drop by the nozzle. When the element resumes its initial shape, it pumps in the reservoir the ink necessary for new printings. The row of nozzles is thus used to generate a column matrix, so that no deflection of the drop is necessary. One variation of this system consists in replacing the piezoelectric crystals by small heating elements behind each nozzle. The drops are ejected following the forming of bubbles of solvent vapor. The volume increase enables the expulsion of the drop. Finally, there is a pulsed inkjet system in which the ink is solid at ambient temperature. The print head thus has to be heated so that the ink liquefies and can print. This enables rapid drying on a wider range of products than conventional systems.

There now exist new "inkjet" printers capable of producing photographic images of excellent quality. However, they cannot supply good proofs if inferior quality printing paper is used. The choice of printing paper is fundamental for the quality of obtained image. The printing paper must combine the following properties: a printed image of high quality, rapid drying after printing, a smooth glossy appearance, and good resistance of the image colors in time, which means especially good stability to ozone present in the atmosphere of the ink dyes.

In general, the printing paper comprises a support coated with one or more layers according to the properties required. Two main technologies have been developed. On the one hand, there is a non-porous printing paper, usually comprising layers of polymers, such as gelatin. This paper enables images that are glossy and ozone stable to be obtained because, once the polymer layer is dry, permeability to ozone is low. However, these papers, not being porous, have to swell to absorb the ink. This swelling slows ink absorption so that the ink can easily run just after printing.

Another paper has been developed to obtain a paper with rapid drying in order to increase printing output rates. This is a paper comprising a porous ink-receiving layer including colloidal particles used as receiving agent and

a polymer binder. This porous paper absorbs the ink rapidly thanks to the pores existing between the particles.

The purpose of the receiving agent is to fix the dyes in the printing paper. The best-known inorganic receivers are colloidal silica or boehmite. For example, the European Patent Applications EP-A-976,571 and EP-A-1,162,076 describe materials for inkjet printing in which the ink-receiving layer contains as inorganic receivers Ludox™ CL (colloidal silica) marketed by Grace Corporation or Dispal™ (colloidal boehmite) marketed by Sasol. However, printing paper comprising a porous ink-receiving layer can have poor ozone stability in time, which is demonstrated by a loss of color density. In particular this is due to the fact that the colloidal particles are easily accessible to ozone and the surface of these particles could catalyze the ozone degradation of the ink dyes.

To meet new market needs in terms of printing speed and color stability to ozone, it is necessary to propose a method enabling improvement of the ozone stability of a material intended for inkjet printing.

SUMMARY OF THE INVENTION

The present invention relates to the use of at least one sulfonic polystyrene or one of its sulfonate salts in an inkjet recording element, said element comprising a support and at least one ink-receiving layer including at least one hydrosoluble binder and inorganic fillers, for improving the ozone stability of said element.

In preference, one uses sulfonic polystyrene in salt form chosen from among the group consisting of sodium polystyrene sulfonate, lithium polystyrene sulfonate, ammonium polystyrene sulfonate, and potassium polystyrene sulfonate.

The use of sulfonic polystyrene or polystyrene sulfonate enables the ozone stability of a porous inkjet recording element to be improved for inkjet printing while obtaining an element having at least the same ink instant-dryness.

BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1, 2, 4 to 8, and 10 to 14 represent the percentage of color density loss for various elements exposed to ozone, and

Figures 3 and 9 represent the percentage of instant dryness for various elements.

DETAILED DESCRIPTION OF THE INVENTION

An inkjet recording element comprises firstly a support. This support is selected according to the desired use. It can be a transparent or opaque thermoplastic film, in particular a polyester base film such as polyethylene terephthalate; cellulose derivatives, such as cellulose ester, cellulose triacetate, cellulose diacetate; polyacrylates; polyimides; polyamides; polycarbonates; polystyrenes; polyolefines; polysulfones; polyetherimides; vinyl polymers such as polyvinyl chloride; and their mixtures. The support used in the invention can also be paper, both sides of which may be covered with a polyethylene layer. When the support comprising the paper pulp is coated on both sides with polyethylene, it is called Resin Coated Paper (RC Paper) and is marketed under various brand names. This type of support is especially preferred to constitute an inkjet recording element. The side of the support that is used can be coated with a very thin layer of gelatin or another composition to ensure the adhesion of the first layer on the support. To improve the adhesion of the ink-receiving layer on the support, the support surface can also have been subjected to a preliminary treatment by Corona discharge before applying the ink-receiving layer.

An inkjet recording element then comprises at least one ink-receiving layer including at least one hydrosoluble binder. Said hydrosoluble binder can be a hydrophilic polymer such as polyvinyl alcohol, poly(vinyl pyrrolidone), gelatin, cellulose ethers, poly(oxazolines), poly(vinylacetamides), poly(vinyl acetate/vinyl alcohol) partially hydrolyzed, poly(acrylic acid), poly(acrylamide), sulfonated or phosphated polyesters and polystyrenes, casein, zein, albumin, chitin, dextran, pectin, derivatives of collagen, agar-agar, guar, carragheenane, tragacanth, xanthan and others. In preference, one uses gelatin or polyvinyl alcohol. The gelatin is that conventionally used in the photographic field. Such a gelatin is described in Research Disclosure, September 1994, No. 36544, part II A. *Research Disclosure* is a publication of Kenneth Mason Publications Ltd., Dudley House, 12 North Street, Emsworth, Hampshire PO10

7DQ, United Kingdom. The gelatin can be obtained from SKW and the polyvinyl alcohol from Nippon Gohsei, or Air Product with the name Airvol® 130.

The ink-receiving layer also comprises, as receiving agent, inorganic fillers. In one embodiment, said inorganic fillers are based on metal oxide or metal hydroxide. In preference, the inorganic fillers are based on alumina, silica, titanium, zirconium, or their mixtures. Preferably, the inorganic fillers are chosen from among the group consisting of the boehmites, fumed aluminas, colloidal silicas, fumed silicas, calcium silicates, magnesium silicates, zeolites, kaolin, bentonite, silicon dioxide, and titanium dioxide. According to another embodiment, the inorganic fillers are based on calcium carbonates, or baryum carbonates.

The quantities of the inorganic fillers and hydrosoluble binder are those generally used for porous inkjet recording elements.

Those skilled in the art know that such inorganic fillers, used alone as a receiving agent in ink-receiving layers, do not enable the required ozone stability of the image to be obtained for inkjet recording elements.

According to the present invention, the use of at least one sulfonic polystyrene or polystyrene sulfonate salt enables the ozone stability of the dyes making up the image to be improved.

Such sulfonic polystyrenes or polystyrene sulfonates are polymers marketed for example by Alco Chemical™ under the VERSA-TL® brand, and can have a molecular weight between 15,000 and 1,000,000.

When polystyrene sulfonate is used, it can be chosen from among the group consisting of sodium, lithium, ammonium and potassium polystyrene sulfonate.

The quantity of sulfonic polystyrene or polystyrene sulfonate (in dry state) is between 0.1% and 10% by weight with reference to the total weight of the wet receiving layer. Preferably, the quantity of sulfonic polystyrene or polystyrene sulfonate (in dry state) is between 0.25% and 8% by weight with reference to the total weight of the wet receiving layer. Still more preferably, the quantity of

sulfonic polystyrene or polystyrene sulfonate (in dry state) is between 1% and 3% by weight with reference to the total weight of the wet receiving layer.

The sulfonic polystyrene or polystyrene sulfonate is added to the layer composition intended to be coated on the support to constitute the ink-receiving layer of the element described above. To produce this composition, in preference, the sulfonic polystyrene or polystyrene sulfonate in the form of an aqueous solution and the inorganic fillers are first mixed together and then the hydrosoluble binder is added. The composition then has the form of an aqueous solution or a dispersion containing all the necessary components.

The composition can be layered on the support according to any appropriate coating method, such as blade, knife or curtain coating. The composition is applied with a thickness between approximately 100 µm and 200 µm in the wet state. The ink-receiving layer has a thickness usually between 5 µm and 50 µm in the dry state. The composition forming the ink-receiving layer can be applied on both sides of the support. It is also possible to provide an antistatic or anti-winding layer on the back of the support coated with the ink-receiving layer.

The inkjet recording element can comprise, besides the ink-receiving layer described above, other layers having another function, arranged above or below said ink-receiving layer. The ink-receiving layer as well as the other layers can comprise all the other additives known to those skilled in the art to improve the properties of the resulting image, such as surface-actives, UV ray absorbers, optical brightening agents, antioxidants, plasticizers, etc.

The use of sulfonic polystyrene or polystyrene sulfonate in an inkjet recording element comprising an ink-receiving layer including inorganic fillers enables the ozone stability of the ink dyes to be improved, without degrading the element drying properties. This invention can be used for any type of inkjet printer as well as for all the inks developed for this technology.

The following examples illustrate the present invention without however limiting the scope.

1) Preparing compositions intended to be layered on a support to constitute an ink-receiving layer

As hydrosoluble binder, polyvinyl alcohol was used (Gohsenol™ GH23 marketed by Nippon Gohsei) diluted to 9% in osmosis water.

The polystyrene was used in the form of two sulfonate salts as given in Table I below and marketed by Alco Chemical™:

Table I

Polystyrene sulfonate	Salt	Form	Molecular weight
Versa TL® 502	Sodium salt	solid	1,000,000
Versa TL® 73	Lithium salt	Solution at 30% in water	70,000

The inorganic fillers used are given below in Table II:

Table II

Inorganic filler	Brand	Charge	Supplier
Fumed alumina (dispersion at 40%)	CAB-O-SPERSE® PG003	Positive	Cabot Corporation
Colloidal silica (dispersion at 40%)	Ondeo Nalco®2329	Negative	Ondeo Nalco Corporation
Colloidal silica (dispersion at 30%)	Ludox™ PGE	Negative	Grace Corporation

All the compositions resulted from mixing:

0 g to 5 g dry polystyrene sulfonate (see Table III below)

13.5 g dry inorganic fillers

18.1 g polyvinyl alcohol in aqueous solution at 9%

Water to 100 g

First the mixture of polystyrene sulfonate in aqueous solution and the inorganic fillers was made in a glass bottle comprising glass beads with diameter 10 mm. The mixture was stirred for three hours on a roller stirrer. Then the polyvinyl alcohol was added and stirred for 18 hours on a roller stirrer. Before

being layered, the resulting mixture was put into a tank thermostatically controlled to 50°C to lower the viscosity of said mixture.

2) Preparing inkjet recording elements

To do this, a Resin Coated Paper type support was placed on a coating machine, first coated with a very thin gelatin layer, and held on the coating machine by vacuum. This support was coated with a composition as prepared according to paragraph 1 using a filmograph to obtain a wet thickness of 200 µm. Then, it was left to dry overnight at ambient air temperature (21°C).

The resulting materials correspond to the examples shown in Table III below giving the polystyrene sulfonate and the quantity used in the ink-receiving layer, as well as the inorganic filler used:

Table III

Material	Inorganic filler added to the ink-receiving layer	Polystyrene sulfonate (PSS)	% by weight of dry PSS in the mixture
Ex 1 (comp.)	Colloidal silica Ludox™ PGE	Versa TL® 502	0
Ex 2 (inv.)	Colloidal silica Ludox™ PGE	Versa TL® 502	0.25
Ex 3 (inv.)	Colloidal silica Ludox™ PGE	Versa TL® 502	1.25
Ex 4 (inv.)	Colloidal silica Ludox™ PGE	Versa TL® 502	2.5
Ex 5 (inv.)	Colloidal silica Ludox™ PGE	Versa TL® 502	5
Ex 6 (comp.)	Colloidal silica Ludox™ PGE	Versa TL® 73	0
Ex 7 (inv.)	Colloidal silica Ludox™ PGE	Versa TL® 73	0.25
Ex 8 (inv.)	Colloidal silica Ludox™ PGE	Versa TL® 73	1.25
Ex 9 (inv.)	Colloidal silica Ludox™ PGE	Versa TL® 73	2.5
Ex 10 (inv.)	Colloidal silica Ludox™ PGE	Versa TL® 73	5
Ex 11 (comp.)	Colloidal silica Nalco®2329	Versa TL® 502	0
Ex 12 (inv.)	Colloidal silica Nalco®2329	Versa TL® 502	0.25
Ex 13 (inv.)	Colloidal silica Nalco®2329	Versa TL® 502	0.5
Ex 14 (inv.)	Colloidal silica Nalco®2329	Versa TL® 502	1
Ex 15 (inv.)	Colloidal silica Nalco®2329	Versa TL® 502	3
Ex 16 (comp.)	Colloidal silica Nalco®2329	Versa TL® 73	0
Ex 17 (inv.)	Colloidal silica Nalco®2329	Versa TL® 73	0.25
Ex 18 (inv.)	Colloidal silica Nalco®2329	Versa TL® 73	0.5
Ex 19 (inv.)	Colloidal silica Nalco®2329	Versa TL® 73	1
Ex 20 (inv.)	Colloidal silica Nalco®2329	Versa TL® 73	3
Ex 21 (comp.)	Fumed alumina CAB-O-SPERSE® PG003	Versa TL® 502	0
Ex 22 (inv.)	Fumed alumina CAB-O-SPERSE® PG003	Versa TL® 502	0.25
Ex 23 (inv.)	Fumed alumina CAB-O-SPERSE® PG003	Versa TL® 502	0.5
Ex 24 (inv.)	Fumed alumina CAB-O-SPERSE® PG003	Versa TL® 502	1
Ex 25 (comp.)	Fumed alumina CAB-O-SPERSE® PG003	Versa TL® 73	0
Ex 26 (inv.)	Fumed alumina CAB-O-SPERSE® PG003	Versa TL® 73	0.25
Ex 27 (inv.)	Fumed alumina CAB-O-SPERSE® PG003	Versa TL® 73	0.5
Ex 28 (inv.)	Fumed alumina CAB-O-SPERSE® PG003	Versa TL® 73	1
Ex 29 (inv.)	Fumed alumina CAB-O-SPERSE® PG003	Versa TL® 73	3

3) Evaluating the ozone stability of the image over time

To evaluate ozone stability over time, a color alteration test by exposure to ozone was performed for each resulting inkjet recording element. For this, targets composed of four colors, cyan, magenta, yellow and black were printed on each element using a KODAK® PPM 200 printer and related ink and/or an Epson® 670 or Epson® 890 printer and related inks, to test equally the various dyes in the inks. The targets were analyzed using a Gretag Macbeth Spectrolino densitometer that measured the intensity of the various colors. Then the elements were placed to the dark in a room with controlled ozone atmosphere (60 ppb) for several weeks. Each week, any degradation of the color density was monitored using the densitometer.

4) Evaluating the instant dryness

Also measured for certain resulting elements was the instant dryness of the ink once printed on said elements.

For this, a target made of 10-cm long strips of four colors, cyan, magenta, yellow and black, was printed on certain of the resulting elements. Just at the end of printing, a sheet of plain paper was put onto the freshly printed target and pressure was applied using a smooth heavy roller. The sheet of plain paper was then removed and the intensity of the transferred image of the target was measured on said sheet. The more intense the transferred image was, the slower the instant dryness of the ink was.

The instant dry percentage is defined by the following equation:

$$\%Dry = \left(1 - \frac{1 - 10^{-D_{mes}}}{1 - 10^{-D_{ref}}} \right) \times 100$$

where D_{mes} is the optical density measured on the image of the transferred target less D_{min} (density of the resulting element not printed)

D_{ref} is the optical density measured on a target printed on the sheet of plain paper less D_{min} .

The optical densities were measured using the Gretag Macbeth Spectrolino densitometer.

The change in the instant dry percentage is linked to the instant dryness of the ink. The higher the percentage %Dry is, the better the instant dryness of the ink is.

5) Results

Figure 1 represents the percentage of density loss observed for the maximum density for the four colors of the target after three weeks for examples 1 to 5 printed using the Kodak® PPM200 printer. Letters C, M, Y and K represent the colors cyan, magenta, yellow and black respectively.

Figure 2 represents the percentage of density loss observed for the maximum density for the four colors of the target after three weeks for examples 1 to 5 printed using the Epson® 890 printer.

Figure 3 represents the instant dry percentage %Dry for the colors, cyan, magenta and black, for the examples 1 to 5 printed using the Epson® 890 printer.

Figure 4 represents the percentage of density loss observed for the maximum density for the four colors of the target after four weeks for examples 6 to 10 printed using the Kodak® PPM200 printer.

Figure 5 represents the percentage of density loss observed for the maximum density for the four colors of the target after four weeks for examples 6 to 10 printed using the Epson® 670 printer.

These Figures 1 to 5 show that the use of polystyrene sulfonate (Versa TL® 502 or Versa TL® 73), in an inkjet recording element comprising an ink-receiving layer including colloidal silica Ludox™ PGE as inorganic receiving agent, enabled the ozone stability of the dyes to be increased considerably, even when very little polystyrene sulfonate was used.

Further, Figure 3 shows that the instant dry percentage is also considerably increased. The use of polystyrene sulfonate did not degrade the instant dryness of the ink but, quite the opposite, enabled it to be improved compared with the element not containing polystyrene sulfonate.

Figure 6 represents the percentage of density loss observed for the maximum density for the four colors of the target after five weeks for examples 11 to 15 printed using the Kodak® PPM200 printer.

Figure 7 represents the percentage of density loss observed for the maximum density for the four colors of the target after five weeks for examples 11 to 15 printed using the Epson® 670 printer.

Figure 8 represents the percentage of density loss observed for the maximum density for the four colors of the target after three weeks for examples 16 to 20 printed using the Kodak® PPM200 printer.

Figure 9 represents the percentage of density loss observed for the maximum density for the four colors of the target after three weeks for examples 16 to 20 printed using the Epson® 890 printer.

Figure 10 represents the instant dry percentage %Dry for the colors, cyan, magenta and black, for the examples 16 to 20 printed using the Epson® 890 printer.

These Figures 1 to 6 show that the use of polystyrene sulfonate (Versa TL® 502 or Versa TL® 73), in an inkjet recording element comprising an ink-receiving layer including colloidal silica Nalco® 2329 as inorganic receiving agent, enabled the ozone stability of the dyes to be increased considerably, in particular when 1% to 3% polystyrene sulfonate was used.

Further, Figure 10 shows that the instant dry percentage of instantly dry ink was also considerably increased when 1% to 3% polystyrene sulfonate was used. The use of polystyrene sulfonate did not degrade the instant dryness of the ink but, quite the opposite, enabled it to be improved compared with the element not containing polystyrene sulfonate.

Figure 11 represents the percentage of density loss observed for the maximum density for the four colors of the target after three weeks for examples 21 to 24 printed using the Kodak® PPM200 printer.

Figure 12 represents the percentage of density loss observed for the maximum density for the four colors of the target after three weeks for examples 21 to 24 printed using the Epson® 890 printer.

Figure 13 represents the percentage of density loss observed for the maximum density for the four colors of the target after three weeks for examples 25 to 29 printed using the Kodak® PPM200 printer.

Figure 14 represents the percentage of density loss observed for the maximum density for the four colors of the target after three weeks for examples 25 to 29 printed using the Epson® 890 printer.

These Figures 11 to 14 show that the use of polystyrene sulfonate (Versa TL® 502 or Versa TL® 73), in an inkjet recording element comprising an ink-receiving layer including fumed alumina as inorganic receiving agent, enabled the ozone stability of the dyes to be increased, in particular when 1% to 3% polystyrene sulfonate was used.